

KORHNO, Yuriy Arsen'yevich; LEBEDINSKAYA, Anna Abramovna; MEN',  
Sof'ya Mikhaylovna; SERGIYENKO, Lyudmila Andreyevna;  
FELIKSON, Anna Moiseyevna; SHAGIYAN, Valentina  
Fedorovna; YENIKOLOPOV, N.S., doktor khim. nauk,  
retsenzent

[Polyformaldehyde] Poliformal'degid. Kiev, Tekhnika,  
1964. 90 p. (MIRA 18:1)

L 28437-66 EWI(m)/ENP(j)/I IJP(c) WWH/RM

ACC NR: AP6017976

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INVENTOR: Yenikolopov, N. S.; Karmilova, L. V.; Konareva, G. P.; Plechova, O. A.; Vol'fson, S. A.; Brikenshteyn, A. A.

ORG: none

34  
0

TITLE: Preparative method for heat-resistant<sup>6</sup> copolymers<sup>1</sup> of trioxane<sup>1</sup> Class 39, No. 181808<sup>6</sup>

SOURCE: Izobreteniya, promyshlennyye obraztsey, tovarnyye znaki, no. 10, 1966, 79

TOPIC TAGS: heat resistant copolymer, trioxane, cyclic ether, copolymer

ABSTRACT: An Author Certificate has been issued for a preparative method for heat-resistant copolymers of trioxane and cyclic ethers such as 1,3,6-trioxacyclo-octane, 1,3,7-trioxacyclodecane, or 1,3,8-trioxacyclododecane. The method involves bulk copolymerization of the monomers in the presence of cationic catalysts, first below the mp and then above the mp of the monomers. [BO]

SUB CODE: 07,11/ SUBM DATE: 02Jun64/ ATD PRESS: 5005

Card 1/1

88

YENIKOLOLOV, S. K.

"The Occurrence of Anopheles Malculipennis in Uninhabited Floodlands of the Sulak River and Data on Seasonal Changes in the Number of Mosquitoes in Dagestan", Med. Paraz. i Paraz. Bolez., Vol. 17, No. 2, pp 168-70, 1948.

YENIKOLOPOV, S.K.

Behavior characteristics of *Anopheles hyrcanus* pall. Med.paraz.  
i paraz.bol. no.1:31-33 Ja-Mr '54. (MLRA 7:3)

1. Iz Dagestanskogo instituta epidemiologii i mikrobiologii  
(direktor instituta Ye.Ye.Zhadkevich). (Mosquitoes)

GERASIMOV, I.P., akademik, otv.red.; ANTIPOV-KARATAYEV, I.N., akademik,  
otv.red.; YENIKOV, K.Kh., dotsent, otv.red.; TANOV, Ye.N.,  
starshiy nauchnyy sotrudnik, otv.red.; GALEVA, Y.V., red.;  
TYURIN, I.V., red.; KAVUN, P.K., red.isd-va; MAKUNI, Ye.V.,  
tekhn.red.

[Soils of Bulgaria] Pochvy Bolgarii. Moskva, 1959. 398 p.  
(MIRA 12:6)

1. Akademiya nauk SSSR. Pochvennyy institut im. V.V.Dokuchayeva.
2. AN Tadzhikskoy SSR (for Antipov-Karatayev).  
(Bulgaria--Soils)

YENIKOLOPYAN N. S.

238T14

USSR/Chemistry - Fuels  
Combustion

Aug 52

"Periodic Combustion Flashes in Mixtures of Carbon Monoxide and Oxygen," N. S. Yenikolopyan and A. B. Nalbandyan

"DAN SSSR" Vol 85, No 6, pp 1309-1312

A quant description of the combustion observed in a mixt of CO and O<sub>2</sub> when a small amount of H is added by diffusion is worked out on the basis of the reaction mechanism and the consts of elementary reactions calcd from previous work.

238T14

When the pressure of the H on the membrane is decreased and its rate of entry to the mixt is decreased, the time between explosions is increased. By means of eqs derived from the mechanism of the reaction, the article explains why the combustion is only a flash and not a complete burning of the entire mixt. Presented by Acad N. N. Semenov 14 Jun 52

238T14

YENIKOLOPYAN, N.S.

Theory of degenerate branching chains. Part 1. Kinetic equations or reactions with degenerate chain branching (with English summary in insert). Zhur.fiz.khim. 30 no.4:769-783 Apr. '56. (MLRA 9:9)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva.  
(Chemical reaction, Rate of)

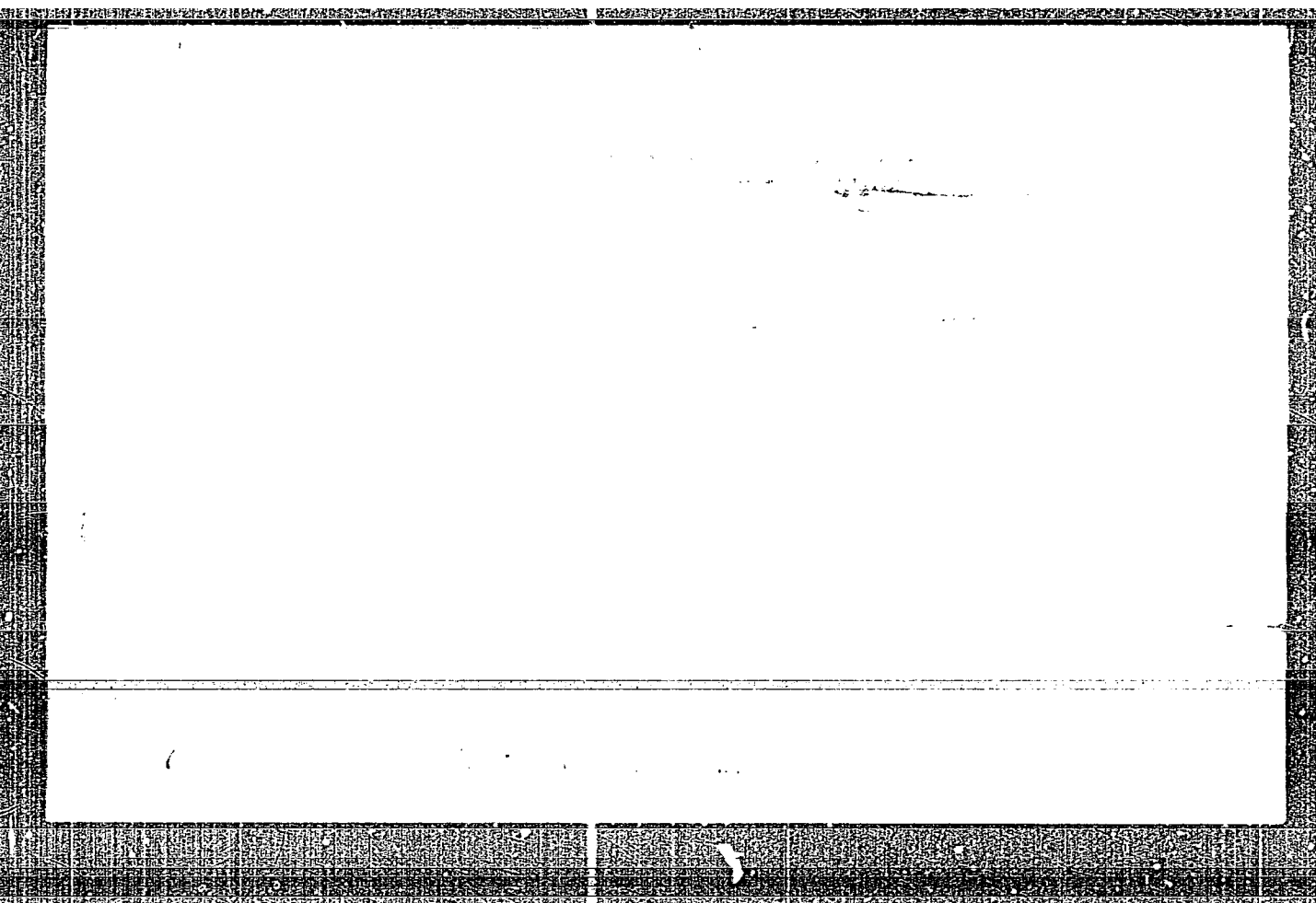
Figure 1. Kinetic curves of the initial stage of oxidation of CH<sub>3</sub>COOH.

data from the temp. relation of the kinetic curve. AUC LOW



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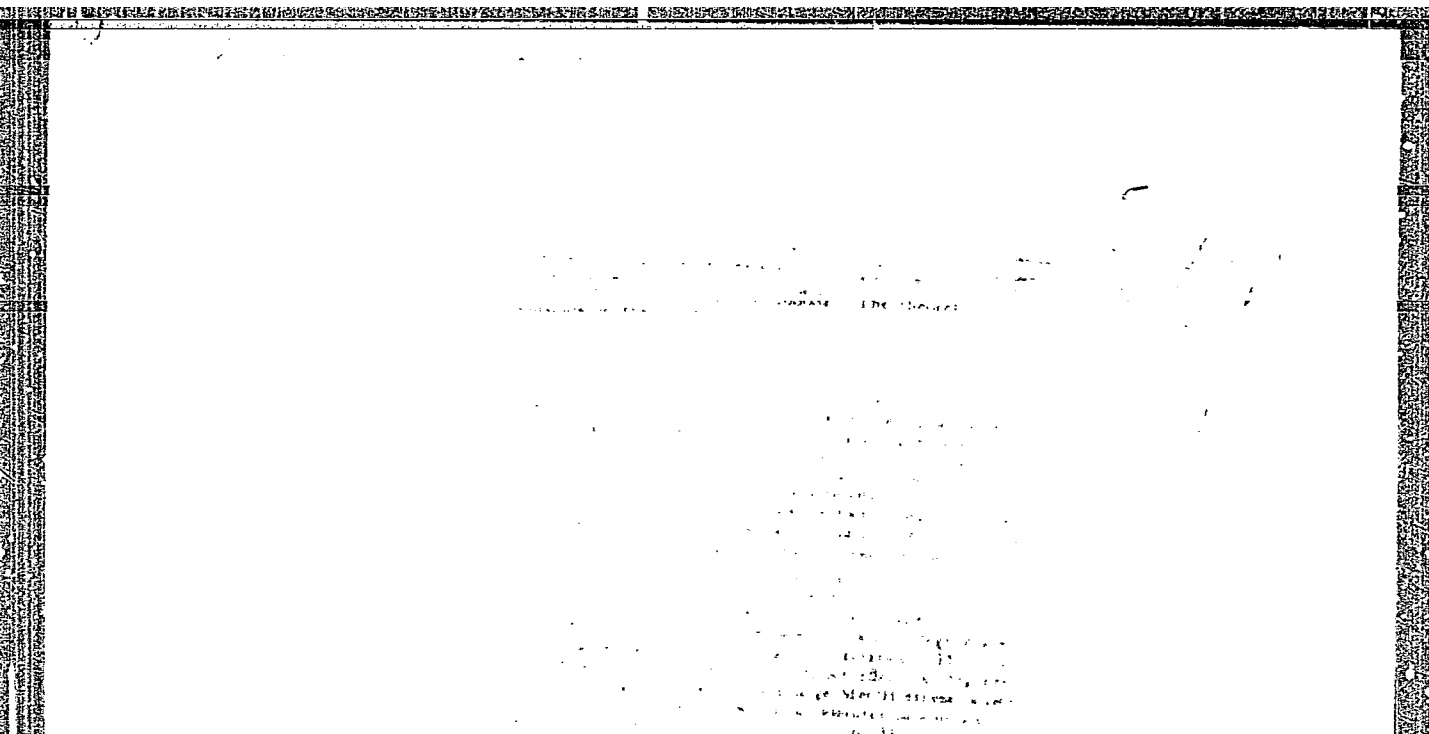
YENIKOLOPYAN, N.S.

Discussion, Probl. kin, i kat, 9:135-137 '57.  
(Oxidation) (Methane)

(MIRA 11:3)

"APPROVED FOR RELEASE: 09/01/2001

CIA-RDP86-00513R001962710004-1



APPROVED FOR RELEASE: 09/01/2001

CIA-RDP86-00513R001962710004-1"

also branching, the addition of a large MeOH excess causes  
solid, HCHO formation and a decrease in the rate of  
the reaction.

YENIKOLOPYAN, G.V.

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-  
chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimii, No 3, 1958, 7184.

Author : N.S. Yenikolopyan, G.V. Korolev, G.P. Savushkina.

Inst :

Title : Upon the Maximum Concentrations of Stable Intermediary Pro-  
ducts in Composite Chain Reactions.

Orig Pub: Zh. fiz. khimii, 1957, 31, No 4, 865-873.

Abstract: It is shown for composite chain reactions of the type  $A \rightarrow B \rightarrow C$  proceeding in two stages (chain formation of a stable intermediary product B from the initial substances A and chain expenditure of B with the formation of final substances C) that there is a proportionality  $n_1 = \alpha_{1j} n_j$  (1) among the concentrations (n) of all active centers (AC) in the reaction system; in this equation,  $\alpha_{1j}$  does not depend on the rates of AC generation (W), of their ramification (a) and of their destruction (g). Should a slowly re-

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Card : 1/3

-1-

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 3, 1958, 7184.

acting AC spontaneously generate, the equation (1) would be right only in the case of long enough chains. It is shown that the stationary concentration of B does not depend on AC concentration in the reaction system, i.e. that it does not depend on W, a and g. It was revealed at the oxidation of  $\text{CH}_4$  (which proceeds following the composite chain mechanism  $\text{CH}_4 \rightarrow \text{CH}_2\text{O} \rightarrow \text{final substances}$ ) at 462 to 525° and the pressure of 53 mm of merc. col. in the mixture  $\text{CH}_4:2\text{O}_2$  that varying the conditions influencing W and g (concentration of the homog. initiator  $\text{NO}_2$ , vessel diameter, dilution of the mixture 8 times with  $\text{N}_2$ , different chemical treatment of the vessel walls) results in great changes of  $\text{CH}_4$  oxidation rate (v), which is the criterion of AC concentration in the reaction system, but does not practically influence the stationary  $\text{CH}_2\text{O}$  concentration. The experiments were carried out under static conditions, v was measured manometrically, and  $\text{CH}_2\text{O}$  concentration

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... concentration of  $\text{CH}_2\text{O}$  rises with the temperature  
rise (the activation energy E is 15.6 kcal per mole). E of v(max)  
is 46 kcal per mole.

APPROVED FOR RELEASE: 09/01/2001

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Card : 3/3

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THIS WAY DIRECT THE CHAIN LENGTH OF THE REACTION PROD.  
NOTE AND THE GAS METER

Yenikolopyan, N.S.

AUTHOR: SAYASOV, YU.S., YENIKOLOPYAN, N.S. PA - 2919  
 TITLE: Note on the Diffusion of Active Centres in the Case of a  
 Quadratic Stripping of Chains in the Volume. (O diffusii aktivnykh  
 tsentrov pri kvadratichnom obryve tsepey v ob'yeme, Russian)  
 PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 1, pp 130 - 133  
 (U.S.S.R.)  
 Received: 5 / 1957 Reviewed: 6 / 1957  
 ABSTRACT: The present paper furnishes a solution of the problem of the  
 spatial steady distribution of the forming heterogeneous active  
 centers on the assumption, that they are destroyed in the case  
 of mutual collisions on the surface and in the interior (i.e. in  
 the case of quadratic stripping of the chains). This problem  
 arises e.g. in the case of a mixture of hydrogen with chlorine  
 without admixtures of oxygen. Let the velocity of heterogeneous  
 generation be much greater than the velocity of the homogeneous  
 generation. The reaction is assumed to take place in a container  
 with plane-parallel walls with a distance of  $2l$  between the walls  
 (one-dimensional problem). In that case the spatial distribution  
 of the active centers is described by the differential equation  
 $D(d^2n/dx^2) - k_p(M)n^2 = 0$ . Here  $n(1/cm^3)$  denotes the concentration  
 of the active centers,  $k_p(cm^6/sec)$  the coefficient of recombination,  
 $(M)$   $(1/cm^3)$  the total concentration of the mixture and of the pro-

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Note on the Diffusion of Active Centres in the Case of a Quadratic Stripping of Chains in the Volume. PA - 2919

duets,  $x(\text{cm})$  - the coordinate measured from the center of the container,  $D(\text{cm}^2/\text{sec})$  - the diffusion coefficient of the active centers. The boundary conditions are also given.

The solution of this differential equation can be represented by the elliptic function of WEIERSTRASS:  $s = \wp(u)$ . In the case of small velocities of the heterogeneous generation only few chains form at the walls, and therefore the probability of an interaction in the volume is small. Subsequently the equilibrium of the process of generation and destruction of the active centers is determined. If, however, a great number of chains form at the walls in unit time,  $\bar{n}$  is determined from the equality of the velocity of generation and destruction of the active centers in unit volume of the container. Furthermore the case is investigated in which the concentration  $n$  of the active centers varies considerably in the interior of the container. With the help of the method of the WEIERSTRASS function described here, the diffusion of the active centers for different conditions can be investigated (in which case the quadratic stripping of chains plays an important part. (1 illustration)

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PA - 2919

Note on the Diffusion of Active Centers in the Case of a Quadratic Stripping of Chains in the Volume.

ASSOCIATION: Institute for Physical Chemistry of the Academy of Science of the U.S.S.R.

PRESENTED BY: V.N.KONDRAT'YEV, Member of the Academy

SUBMITTED: 18.10.1956

AVAILABLE: Library of Congress

Card 3/3

ANISONYAN, A.A.; GUDKOV, S.F.; IVANOV, A.K.; YENIKOLOPYAN, N.S.;  
MARKEVICH, A.M.; NALBANDYAN, A.B.

Results of the operation of an experimental apparatus for  
the manufacture of formalin from natural gas. Trudy VNIIGAZ  
no.3:130-142 '58. (MIRA 11:8)  
(Natural gas) (Formaldehyde)

AUTHORS:

Yenikolopyan, N. S., Polyak, S. S., Shtern, V. Ya. 80V/76-32-9-45/46

TITLE:

On the Nature of the "Cold Flame" Phenomenon (O prirode kholodnoplamennogo yavleniya)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 9, pp 2224-2226 (USSR)

ABSTRACT:

Two views are represented in publications on the oxidation of hydrocarbons in regard to the nature of the "cold flame" phenomenon. M. B. Neyman (Ref 1) explains this phenomenon in terms of the explosive decomposition of organic peroxides, while Pease (Ref 2) and Norrish (Refs 3 and 4) explain it as a result of the thermal instability of the reacting system. The authors suggest a new mechanism. He holds that the peroxide radical reacts in one of two possible ways: either with the initial hydrocarbon ( $RO_2^\bullet + RH \rightarrow ROOH + R^\bullet$ ), or through molecular decomposition ( $RO_2^\bullet \rightarrow R'CHO + R''O^\bullet$ ). The second reaction becomes predominant with an increase in temperature. To explain this phenomenon an idea of N. N. Semenov (Ref 5) was used. This is the so-called "degenerated branching":  $R'COH + RO_2 \rightarrow$

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On the Nature of the "Cold Flame" Phenomenon

SOV/76-32-9-45/46

—  $RO^{\bullet} + O^{\bullet}H + R'CO^{\bullet}$ . Because of the action of the above-mentioned mechanisms there is a temperature range in which the optimal conditions for "branching" exist. There are 12 references, 8 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva (AS USSR, Moscow Institute of Chemical Physics)

SUBMITTED: January 31, 1958

Card 2/2

AUTHORS: Yenikolopyan, N. S., Korolev, G. V. 20-118-6-25/43

TITLE: Formaldehyde and Acetaldehyde Yields in the Oxidation of Ethane at High Temperatures (O vykhodakh formal'degida i atsetal'degida pri vysokotemperaturnom okislenii etana)

PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol. 118, Nr 6, pp. 1138-1141 (USSR)

ABSTRACT: The conceptions which in complicated chain reactions lead to the existence of extreme yields of stable intermediate products were verified at the example of the oxidation of methane. As sample for the further verification of these conceptions the next more complicated representative of the homologous series of paraffin hydrocarbons, i.e. ethane, was chosen. The behavior of the yields of formaldehyde and acetaldehyde was investigated in the case of variation of the conditions of oxidation of  $C_2H_6$  at high temperatures. The apparatus and the method were described already earlier. The experiments were carried out in two quartz reaction containers with a diameter of 45 mm and a volume of 250 ml, the walls of which were

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Formaldehyde and Acetaldehyde Yields in the Oxidation of Ethane 20-118-6-25/43  
at High Temperatures

treated as follows: 1) by washing with  $\text{H}_2\text{F}_2$  ( $\text{H}_2\text{F}_2$ -container) and 2) by washing with a one percent solution of  $\text{K}_2\text{B}_4\text{O}_7$  ( $\text{K}_2\text{B}_4\text{O}_7$ -container). The results of these experiments at low pressures (25 mm of mercury column) are illustrated in a diagram for mixtures relatively rich in oxygen ( $\text{C}_2\text{H}_6:2\text{O}_2$ ). The addition of an initiator for the radicals ( $\text{NO}_2$ ) and the dilution of the reaction mixture with a rare gas ( $\text{N}_2$ ) increase the concentration of the active centres in the reaction mixture to a great extent. The yield of  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{CHO}$  here remains practically unchanged, i.e. it does not differ from the extreme yields. The same experiments were repeated at a pressure of 53 mm torr. The yield of  $\text{CH}_2\text{O}$  remains unchanged as before in the case of a modification of the concentration of the active centres. However, the velocity of the accumulation of  $\text{CH}_3\text{CHO}$  increases considerably in the very last moments of transformation. The concentration reaches

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Formaldehyde and Acetaldehyde Yields in the Oxidation of Ethane<sup>20</sup>-118-6-25/43  
at High Temperatures

its maximum if the transformation velocity already equals zero with respect to  $\Delta p$ . Then the extreme yields of the stable intermediate product are investigated in a complicated chain reaction. The maximum yield of  $\text{CH}_3\text{CHO}$  suffers no systematic modification in the case of concentration changes of the active centres in the reaction system. In the case of the mixture  $2\text{C}_2\text{H}_6:\text{O}_2$  the yield of  $\text{CH}_2\text{O}$  becomes a function of the reaction conditions: the conditions leading to the concentration increase of the active centres in the system increase the yield of  $\text{CH}_2\text{O}$ .

There are 4 figures and 2 references which are Soviet

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR  
(Institute of Chemical Physics, AS USSR)

PRESENTED: July 30, by N. N. Semenov, Member, Academy of Sciences USSR

SUBMITTED: July 27, 1957

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20-118-5-38/59

AUTHORS: Yenikolopyan, N. S. , Korolev, G. V.

TITLE: Formaldehyde Yields on Methane Oxidation, as Dependent Upon the Homogeneous Initiator Concentration, Inert Gas Admixtures and the Condition of the Reaction Vessel Walls (Zavisimost' vykhodov formal'degida pri okislenii metana ot kontsentratsii gomogennogo initsiatora, dobavok inertnogo gaza i ot sostoyaniya stенок reaktsionnogo sozuda)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp.983-986 (USSR)

ABSTRACT: The apparatus and the method of the measurements were described by the same authors already earlier (Ref 1). Experiments on the not initiated oxidation of  $CH_4$  were carried out in quartz reaction containers of the same diameter (45 mm) the surface of which was processed in different way: 1) No special processing ("pure" container); 2) washed out by means of hydrofluoric acid ( $H_2F_2$  container); 3) washed out by means of a 1 % solution of  $K_2B_4O_7$  ( $K_2B_4O_7$  container). The results of

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20-118-5-38/59

Formaldehyde Yields on Methane Oxidation, as Dependent Upon the Homogeneous Initiator Concentration, Inert Gas Admixtures and the Condition of the Reaction Vessel Walls

these experiments are illustrated on a diagram and demonstrate that the yield of  $\text{CH}_2\text{O}$  depends on the state of the surface of the reaction container. Therefore, yield of  $\text{CH}_2\text{O}$  at given conditions of the oxidation of  $\text{CH}_4$  has no maximum, i.e. velocity of molecular consumption of  $\text{CH}_2\text{O}$  is of the same order of magnitude as with the consumption in the chain reaction. The dependence of the yield of  $\text{CH}_2\text{O}$  on the nature of the surface of the reaction container observed here may have two reasons: 1) Destruction of the active centers on the surface of the reaction container takes place in the kinetic or diffusion-kinetic range. 2) Heterogeneous reaction of the consumption of  $\text{CH}_2\text{O}$  takes place in the kinetic or diffusion-kinetic range. A dilution of the reaction compound with nitrogen renders difficult the diffusion of the radicals and  $\text{CH}_2\text{O}$  molecules to the wall and therefore is bound to increase the yield of  $\text{CH}_2\text{O}$ . The admixture of materials which can produce active centers to the reaction compound is equally bound to increase the yield of  $\text{CH}_2\text{O}$ . A diagram illustrates the results of the experiments on the oxidation of methane under the presence of different amounts of  $\text{NO}_2$ . Thus, e.g.

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Formaldehyde Yields on Methane Oxidation, as Dependent Upon the Homogeneous Initiator Concentration, Inert Gas Admixtures and the Condition of the Reaction Vessel Walls

an increase of the  $\text{NO}_2$ -content in the compound from 0 to 0,2 - 0,3 % increases the yield of  $\text{CH}_2\text{O}$  by 4 to 8 times. At the same time a strong increase of oxidation velocity is observed. With sufficiently high concentration of the active centers in the reaction system the yield of the stable intermediary product reaches the maximum value. Variation of the concentration of the initiator exerts strong influence on the oxidation velocity, however, practically does not influence at all the yield of  $\text{CH}_2\text{O}$ . All results found here show among others the following: In the case of a not initiated oxidation of methane formaldehyde is consumed molecularly and the velocity of this consumption has the same order of magnitude as consumption in chain reaction. There are 4 figures and 1 reference, 1 of which is Soviet.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute for Physical Chemistry AS USSR)

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Formaldehyde Yields on Methane Oxidation, as Dependent Upon the Homogeneous  
Initiator Concentration, Inert Gas Admixtures and the Condition of the Re-  
action Vessel Walls 20-118-5-38/59

PRESENTED: July 30, 1957, by N. N. Semenov, Member, Academy of Sciences,  
USSR

SUBMITTED: July 30, 1957

Card 4/4

AUTHOR: Yenikolopyan, N. S. 20-119-3-35/65

TITLE: On the Negative Temperature Coefficient in the Oxidation of Hydrocarbons (Ob otritsatel'nom temperaturnom koeffitsiyente pri okislenii uglevodorodov)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 3, pp. 520-522 (USSR)

ABSTRACT: A characteristic peculiarity of the oxidation of the hydrocarbons is the so called negative temperature coefficient in a certain temperature range. This negative temperature range has a strong influence upon the kinetics of the slow oxidation and upon the character of the self-ignition of the hydrocarbons. The present theories (references 6,12,13,14) actually do not explain the phenomena of the negative temperature coefficient. This work investigates on the basis of the theory of the degenerate ramification by N. N. Semenov the negative temperature coefficient as a result of the competition of the elementary processes, which are participating in a composed chain reaction. At low temperatures the oxidation of the hydrocarbons goes on passing through superoxide radicals, which form after the reaction  $R + O_2 \rightarrow ROO$ . This process has a low steric factor ( $10^{-3}$  to  $10^{-4}$ ) and a low activation energy

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On the Negative Temperature Coefficient in the Oxidation of 2o-119-3-35/65  
Hydrocarbons

(2 to 4 great calories/mol). The elementary process of the degenerate ramification can be represented, after B. L'yuis and G. El'be (reference 13) as well as after V. V. Voyevodskiy and V. I. Vedeneyev (reference 16), as result of the interaction of the superoxide radical with a stable intermediary product (e.g. with aldehyde):  $ROO + R'CHO \rightarrow RO + OH + R'CO$ . By this reaction 3 new active centers form from a radical. The reaction  $ROO \rightarrow R'CHO + R''O$  takes place with previous isomerization of the superoxide radical and therefore it has a high activation energy (20 great calories/mol). The competition of the two above given reactions causes the maximum in the dependence of the reaction velocity on the temperature. At low temperatures the superoxide radical must react according to the bimolecular reaction. From a certain temperature onwards, however, the monomolecular continuation reaction, which above is given in the second place, predominates, by which the oxidation velocity is decreased. The destruction of the active centers essentially depends on the destruction of the radicals R. With increasing temperature the probability of the ramification decreases and on the other side the steady concentration of the radicals ROO decreases, so that the limiting process is the reaction  $R + O_2 \rightarrow ROO$ . Therefore the oxidation

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velocity of the hydrocarbons rapidly decreases with increasing temperature. On the base of this simplified oxidation scheme an expression for the reaction velocity is written down. The velocity of the oxidation of a hydrocarbon passes a maximum with increasing temperature. The author also solved the following inversion problem: Given are the values of the ratio of certain parameters and of the difference of the activation energy of the elementary reactions. The steric factor of the reaction  $R + O_2 \rightarrow ROO$  is to be computed, so that the reaction velocity has its maximum at the temperature of  $400^\circ C$ . The concerning numerical data are given here. The generalized scheme of the oxidation of the hydrocarbons, suggested here, thus leads to a maximum of the reaction velocity with regard to the temperature. In case of further increase of the temperature the consideration of the reaction  $RCHO + O_2 \rightarrow RCO + HO_2$  leads to an increase of the reaction velocity.

There are 2 figures and 20 references, 11 of which are Soviet.

ASSOCIATION:  
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Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of

On the Negative Temperature Coefficient in the Oxidation of Hydrocarbons 20-119-3-35/65

Chemical Physics, AS USSR)

PRESENTED: September 14, 1957 by V. N. Kondrat'yev, Member , Academy of Sciences, USSR

SUBMITTED: September 11, 1957

AVAILABLE: Library of Congress

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YENIKOLOPYAN, N.S.,

5(3)

PHASE I BOOK EXPLOITATION

SOV/3198

Nalbandyan, Aram Bagratovich, and Nikolay Sargeyevich Yenikolopyan

Formal'degid - material dlya plastmass (Formaldehyde: Raw Material for Plastics) Moscow, AN SSSR, 1959. 68 p. (Series: Akademiya nauk SSSR. Nauchno-populyarnaya sstriya) 17,000 copies printed.

Resp. Ed.: V.N. Kondrat'yev, Academician; Ed. of Publishing House: V.N. Vyazemtaev; Tech. Ed.: A.P. Guseva.

Sponsoring Agency: Akademiya nauk SSSR. Redkollegiya nauchno-populyarnoy literatury.

PURPOSE: This book is intended for chemists interested in plastics production, students of organic chemistry, and persons interested in the theory and practice of synthetic materials production.

COVERAGE: The booklet describes the nature of formaldehyde, its principal properties, methods for its production, and its most important chemical reactions with other substances to produce synthetic resins and plastics.

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Raw Material (Cont.)

SOV/3198

Also, some properties of formaldehyde products, and their industrial and domestic uses are reviewed. No personalities are mentioned. There are 10 Soviet references.

TABLE OF CONTENTS:

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AVAILABLE: Library of Congress

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TM/jb  
2-24-60

5(3)

SOV/80-32-4-38/47

AUTHORS: Yenikolopyan, N.S., Kleymenov, N.A., Karmilova, L.V., Markevich, A.M.  
and Nalbandyan, A.B.

TITLE: The Preparation of Formaldehyde in a Jet Apparatus by Means of the  
Oxidation of Methane Catalyzed by Nitrogen Oxides (Polucheniye formal'-  
degida na struyevoy ustanovke putem okisleniya metana, katalizirovannogo  
okislami azota)

PERIODICAL: Zhurnal prikladnoy Khimii, 1959, Vol 32, Nr 4, pp 913-919 (USSR)

ABSTRACT: The problem of methane oxidation, very important in view of chemical  
utilization of natural gases, was dealt with in many investigations,  
including those of Medvedev [Refs 25, 26] and D.M. Rudkovskiy. The  
present article describes some results of laboratory studies in ob-  
taining formaldehyde by means of methane oxidation catalyzed by nitro-  
gen oxides. The following research workers of the VNIIGAZ MNP parti-  
cipated in individual phases of these studies: S.A. Anisonyan, S.Ya.  
Beyder, and N.I. Vinnikova, and of the Giprokauchuk MKhP: A.S. Zhadayev,  
N.N. Chernov and M.N. Shendrik. The methane oxidation was carried out  
under jet conditions at a pressure of the gas mixture near the atmo-  
spheric one and at temperatures of 600 to 800°C. Various conditions of  
experimentation were tried out in order to find the optimum ones, and  
the results were as follows: 1. The treatment of the inner surface of

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SOV/80-32-4-32/47

The Preparation of Formaldehyde in a Jet Apparatus by Means of the Oxidation of Methane Catalyzed by Nitrogen Oxides

a vessel, in which reactions take place, with  $K_2B_4O_7$  increases and stabilizes the yield of formaldehyde and reduces the reaction temperature by 80 or 100°C; 2. The relative yield of formaldehyde ( $CH_2O : NO$ ) amounts to 10 to 12 molecules per one molecule of the catalyst; 3. The optimum composition of the methane-air mixture was found to be 1 : 2; 4. The optimum temperature of the reaction is about 100°C; 5. The stable run of the reaction is possible in metal vessels; 6. The laboratory results were confirmed by experiments carried out in a pilot installation with a capacity of 13 m<sup>3</sup>/hr of gas-air mixture. There are 7 graphs and 35 references, 16 of which are Soviet, 14 English, 2 German, 1 Swiss, 1 French and 1 Japanese.

SUBMITTED: September 30, 1957

Card 2/2

SOV/80-32-5-35/52

5(3)

AUTHORS: Yenikolopyan, N.S., Kleymenov, N.A., Karmilova, L.V., Markevich, A.M., Naibandyan, A.B.

TITLE: The Preparation of Formaldehyde by Methane Oxidation Reaction Catalyzed by Nitrogen Oxides

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 5, pp 1132-1135 (USSR)

ABSTRACT: The preparation of formaldehyde in reaction vessels installed in line and also by the method of recirculation is investigated here. In one series, the gas-air mixture of 33.3% CH<sub>4</sub>, 66.6% air and 0.1% NO was passed through reaction vessels. The formaldehyde was separated by water in absorbers. It has been shown that under these conditions 7.4% of methane is oxidized to formaldehyde and 9 - 12% to carbon monoxide. In the closed circulation method the mixture was passed many times through the reaction vessel. After 8 cycles 18.5% of methane is oxidized to formaldehyde and 19.7% to carbon monoxide. An additional supply of air or oxygen increases the yield to 32%. The yield of formaldehyde per 1 molecule of NO is 20 and even 30 molecules at 550 and 590°C. In the continuous circulation method the mixture is continuously supplied with fresh gas. The temperature varies from 565 - 680°C. NO was supplied

Card 1/2

SOV/80-32-5-35/52

The Preparation of Formaldehyde by Methane Oxidation Reaction Catalyzed by Nitrogen Oxides

to keep the concentration at 0.1 volume %. After 10 circulations 21% of methane is converted to formaldehyde. The losses of NO due to absorption in the absorber amount to 2-16%. It has been found that NO is not consumed in the reaction. There are 3 graphs, 1 table and 2 Soviet references.

SUBMITTED: September 30, 1957

Card 2/2

SOV/76-33-3-21/41

5(4)

AUTHOR:

Yenikolopyan, N. S.

TITLE:

On the Change of the Order of Reaction With Temperature in the Oxidation of Hydrocarbons (Ob izmenenii poryadka reaktsii s temperaturoy pri okislenii uglevodorodov)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 3, pp 642 - 648 (USSR)

ABSTRACT:

The author of this paper and several others observed that temperature rise in hydrocarbon oxidations (e.g. in the case of methane) leads to an increase in the order of reaction with respect to oxygen (I), and to a decrease of the order of reaction with respect to hydrocarbon (II) (Table 1). This observation was confirmed by data on the minimum pressure of simultaneous ignition as a function of temperature in the case of various compositions of (I)-(II) mixtures. It was thus stated that with rising temperature the dependence of the oxidation rate on (I) increases while the dependence on (II) decreases (Fig 5). Contrary to what was assumed in (Ref 23), (Ref 29), and (Ref 19) it is stated that the kinetics of oxidation is to be explained by stronger "competi-

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On the Charge of the Order of Reaction With Temperature SOV/76-33-3-21/41  
in the Oxidation of Hydrocarbons

tion" of a few elementary processes at rising temperature.

The monomolecular reaction  $ROO^{\cdot} \xrightarrow{k_4} R^{\cdot}CHO + R''O^{\cdot}$ , which exhibits a higher activation energy than the reaction

$R^{\cdot} + O_2 \xrightarrow{k_2} ROO^{\cdot}$ , is strongly accelerated by rising temper-

ature so that at higher temperatures the latter becomes the determining reaction. On the basis of this assumption the author computed the maximum reaction rate of (II) as a function of the concentration of (II) and (I) at various temperatures. In this connection the ramification was assumed to develop according to the mechanism established by N. H. Semenov (Table 2). There are 5 figures, 2 tables, and 31 references, 11 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva  
(Academy of Sciences, USSR, Institute of Chemical Physics,  
Moscow)

SUBMITTED: August 1, 1957

Card 2/2

5.3200  
5.4300

## AUTHORS:

Karmilova, L. V., Yenikolopyan, N. S.,  
Nalbandyan, A. B. (Moscow)

69136

S/076/60/034/03/009/038  
B115/B016

## TITLE:

Kinetics and Mechanism of Methane Oxidation. I. Fundamental  
Macrokinetic Rules

## PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol 34, Nr 3, pp 550 - 558  
(USSR)

TEXT: The papers by N. N. Semenov (Refs 1,2) dealing with the oxidation processes of hydrocarbons are mentioned. In the present paper the results of a thorough investigation of the kinetics and composition of the oxidation products of methane during the entire course of reaction in a vessel with exactly prescribed type of surface are given. The rules in the accumulation of intermediates ( $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$ ), some new phenomena in methane oxidation, and the probable mechanism of the process will be dealt with in the following publications of this series. The experiments were carried out in a static device already previously described (Ref 4). To analyze the formaldehyde and hydrogen peroxide a calorimeter of the type FEK-M was used. The experiments were made in a temperature range of from 423 to 513°C, in a pressure range of from 117 to 375 torr, and at ratios of  $\text{CH}_4:\text{O}_2 = 0.5; 1 \text{ and } 2$  (Figs 1-3), in which connection the

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Kinetics and Mechanism of Methane Oxidation.  
I. Fundamental Macrokinetic Rules

69136

S/076/60/034/03/009/038  
B115/B016

accumulation of reaction products ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ) was pursued. The reaction kinetics in dependence on temperature (Fig 4), and the influence exercised by the composition of the initial mixture and initial pressure upon the kinetics of methane oxidation (Figs 5,6) were pursued. It is pointed out that the maximum rates of the consumption of initial reagents and accumulation of end products of the reaction in the temperature range investigated are in agreement with the stoichiometric ratios. The activation energy of methane oxidation is  $41.5 \pm 1$  kcal/mole. The dependence of the maximum rate of methane consumption on the initial pressure of the reaction mixture and its logarithmic anamorphosis is pursued (Fig 7). The degree of the completeness of the reaction of methane oxidation ( $n = 2.7$ ), the reaction degree for methane ( $\alpha = 1.62$ ), and that for oxygen ( $\beta = 0.96$ ) at a total pressure of  $\gamma \approx 0.1$ , were determined (Figs 8,9). The dependence of the induction period on the pressure of the initial mixture and its logarithmic anamorphosis are given (Fig 10). The temperature coefficient ( $E_{\tau 1} = 36 \pm 1$  kcal/mole) was also determined. The student V. T. Il'in also assisted in this investigation. There are 10 figures and 22 references, 10 of which are Soviet.

Card 2/3

69136

Kinetics and Mechanism of Methane Oxidation.  
I. Fundamental Macrokinetic Rules

S/076/60/034/03/009/038  
B115/B016

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki (Academy of  
Sciences of the USSR, Institute of Chemical Physics)

SUBMITTED: June 5, 1958

Card 3/3

S/076/60/034/05/08/038  
B010/B0025.3400(B)  
5.3200  
AUTHORS:

Karmilova, L. V., Yenikolopyan, N. S., Nalbandyan, A. B.

TITLE:

Kinetics and Mechanism of Methane Oxidation. II. Kinetics  
of Accumulation of Intermediates //

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 5,  
pp. 990-994

TEXT: The investigation under review was conducted with the participation of I. Yu. Uvarova. The authors studied the kinetics of accumulation of formaldehyde and hydrogen peroxide in the methane oxidation in a quartz vessel treated with HF. The influence of temperature was tested with a stoichiometric methane - oxygen mixture at 235 torr pressure and temperatures of 426, 472, 491.5, and 513°C (Figs. 1-4, kinetic curves). The analysis of the curves showed that formaldehyde appears as primary intermediate, while hydrogen peroxide is formed after longer contact times by oxidation of formaldehyde. The maximum concentration of formaldehyde rises with temperature, while that of hydrogen peroxide drops. The yield of hydrogen peroxide drops likewise with a rise in temperature. The activation energy of the formaldehyde formation amounts to  $E(\text{CH}_2\text{O})_{\text{max}} = 7.8 \pm 0.5 \text{ kcal}$ .

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Kinetics and Mechanism of Methane Oxidation.  
 II. Kinetics of Accumulation of  
 Intermediates

S/076/60/034/05/08/038  
 B010/B002

The maximum yield of formaldehyde increases in proportion to a rise in the initial pressure of the gas mixture. While the yield of hydrogen peroxide depends but little on the formaldehyde content in the mixture, the maximum yield of formaldehyde rises linearly with rising methane content in the gas mixture. With ratios  $O_2 : CH_4 = 2$  to 0.86, the maximum yield of formaldehyde is independent of the oxygen content in the gas mixture, whereas in the case of  $O_2 : CH_4 = 0.86$  to 0.128,  $CH_2O_{max}$  drops linearly with dropping oxygen partial pressure. A paper by A. M. Markevich is mentioned in the text. There are 11 figures and 13 references: 8 Soviet and 5 English.

SUBMITTED: June 5, 1958

Card 2/2

11.1000  
5.3200

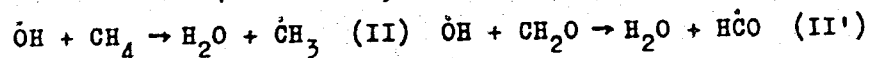
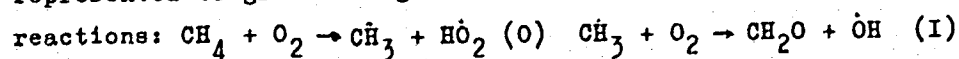
81565  
S/076/60/034/06/04/040  
B015/B061

AUTHORS: Karmilova, L. V., Yenikolopyan, N. S., Malbandyan, A. B.,  
Semenov, N. N. (Moscow)

TITLE: Kinetics and Mechanism of the Oxidation of Methane.  
III. Detailed Mechanism of the Reaction

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 6,  
pp. 1176-1185

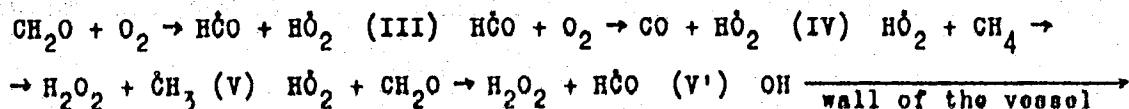
TEXT: On the basis of the kinetic data and the modern conception of the energy of elementary reactions of radicals with stable molecules, a scheme of the most probable oxidation mechanism of methane in the gaseous phase is derived, with due consideration of the branch reaction of formaldehyde in the process. The oxidation mechanism can be represented to greater degrees of conversion by the following system of



Card 1/2

Kinetics and Mechanism of the Oxidation of  
Methane. III. Detailed Mechanism of the  
Reaction

81565  
S/076/60/034/06/04/040  
B015/B061



Calculated data of the maximum rate of oxidation compared with experimental data are given in Table 1 for temperatures of 472°, 491.5° and 513°C, and the values of the kinetic parameters of the methane oxidation in Table 2. The quantitative agreement of the values calculated according to the derived mechanism with those of the experimental data confirm the validity of the proposed reaction mechanism. L. I. Avramenko, A. M. Markevich, and V. V. Voyevodskiy are mentioned in the text. There are 2 tables and 20 references: 14 Soviet, 4 British, and 1 Canadian.

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki (Academy  
of Sciences USSR, Institute of Chemical Physics)

SUBMITTED: June 23, 1958

Card 2/2

87765

S/076/60/034/007/028/042/XX  
B004/B068

5.3400(B)

AUTHORS: Yenikolopyan, N. S. and Bel'govskiy, I. M.  
TITLE: Catalytic Oxidation of Methane and Methyl Alcohol  
PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 7,  
pp. 1571 - 1580

TEXT: The aim of this paper is to establish the reason for the great difference between formaldehyde yields obtained by oxidation of methanol and methane. The experiments were carried out in an ordinary vacuum unit. The reaction vessel was a quartz cylinder 180 mm long and 38 mm in diameter. The following mechanisms were investigated: 1) the kinetics of homogeneous oxidation, with a previous treatment of the walls of the reaction vessel with a 2% aqueous potassium-tetraborate solution, and 2) the kinetics of heterogeneous oxidation with metallic silver vaporized upon the walls of the reaction vessel. By solving the heat-conduction equation, it was established for the homogeneous reaction that at the reaction rates observed (heat-evolution rate and acceleration of the reaction) the system can be considered to be a steady one, and that

Card 1/3

87765

## Catalytic Oxidation of Methane and Methyl Alcohol

S/076/60/034/007/028/042/XX  
B004/B068

the separate calorimetric method developed by A. A. Koval'skiy can be applied. The kinetics of homogeneous oxidation was studied with methane at 580°C, 250 mm Hg,  $\text{CH}_4:\text{O}_2 = 1:1$ , and with methanol at 490°C, 106 mm Hg, and  $\text{CH}_3\text{OH}:\text{O}_2 = 1:1$ . Maximum formaldehyde concentration was found for  $\text{CH}_4$  at 1 mm Hg, and for  $\text{CH}_3\text{OH}$  at 4.7 mm Hg, in accordance with the higher reactivity of methanol. The oxidation of methanol on the silver catalyst was completely heterogeneous and very rapid. Formaldehyde, the intermediate product, is desorbed from the catalyst into the volume of the reaction vessel. The homogeneous oxidation of formaldehyde and methanol is completely suppressed by the rapid destruction of the active centers on the silver surface. The oxidation of methane on the silver catalyst was considerably slower than in the pure vessel.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were formed. The oxidation process was not accelerated by the addition of formaldehyde. From this, it is concluded that the oxidation of  $\text{CH}_4$  on the silver catalyst does not take place through the intermediate stage of formaldehyde formation. There are 8 figures, 3 tables, and 13 references: 12 Soviet and 1 British.

Card 2/3



67765

Catalytic Oxidation of Methane and Methyl Alcohol S/076/60/034/007/028/042/XX  
B004/3068

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki  
(Academy of Sciences USSR, Institute of Chemical Physics)

SUBMITTED: October 18, 1958

X

Card 3/3

19720  
19720

Miller, Y. I., Levin, P. I., Kuznetsov, G. P., Kovalev, W. B., and Zaslavskiy, V. S.

Application of the Kinetic Method of Isotopes for Investigating the Oxidation of Nitroethane in the Presence of Nitroethane

Journal Fizicheskoy Khimii, 1960, Vol. 34, No. 9, pp. 1980-1986

Two of the authors (Ref. 7) observed that in the oxidation of nitroethane with small additions of  $\text{SO}_2$ , a slight temperature rise occurs. The latter is due to the formation of nitroethane, which acts as a catalyst and, at first, decays quickly, then the reaction it maintains a constant concentration for 1-1.5 minutes. For the time of concentration summary of the nitroethane, it may be assumed that nitroethane either does not take part in the reaction, or (which is more probable) it was used in the reaction, but in the same quantity. In the present case, it was found that the kinetic method that the latter assumption is correct. The

$\text{C}^{14}_2\text{H}_5\text{NO}_2$  used was produced from  $\text{NaC}^{14}_2\text{O}_3$  and the  $\text{C}^{14}_2\text{H}_5\text{NO}_2$  from marked acetic acid was obtained by a method developed by P. I. Levin (Ref. 11), and nitroethane was separated by distillation from nitroethane (Table, results of separation). Three series of experiments were carried out: in the first, a mixture of 74.0 torr  $\text{CH}_4$  - 146 torr  $\text{O}_2$  - 4.7 torr  $\text{C}^{14}_2\text{H}_5\text{NO}_2$  was used at a temperature of 475°C. The activity curves (Fig. 2) show that nitroethane is formed from methane, and that nitroethane is not isolated. In the second series of experiments,  $\text{C}^{14}_2\text{H}_5\text{NO}_2$  was utilized besides nitroethane, and it was found that formaldehyde is formed partly from nitroethane and partly from methane (Fig. 3). To explain the part played by  $\text{O}_2$ , a third series was carried out with 120.3 torr  $\text{CH}_4$  - 4.7 torr  $\text{C}^{14}_2\text{H}_5\text{NO}_2$  at 475°C, and it was found that in the presence of  $\text{O}_2$  the maximum concentration of formaldehyde is four times lower, and is attained three times more rapidly. The fraction of formaldehyde not formed from nitroethane, is found by a reaction of nitroethane

with nitrogen oxides. The isotopic exchange between the scheme  
 $\text{C}^{14}_2\text{H}_5\text{NO}_2 + \text{CH}_4 \rightleftharpoons \text{C}^{14}_2\text{H}_5\text{NO}_2 + \text{CH}_4$   
 The formation and consumption rates of nitroethane in the presence and in the absence of oxygen were calculated. 2-3 methane isotopes utilized for every nitroethane molecule. There are 6 figures, 1 table, and 11 references: 10 Soviet and 1 foreign.

ASSOCIATION: Akademiya nauk SSSR Institut Khimicheskoy Fiziki (Academy of Sciences USSR, Institute of Chemical Physics)

SUBMITTED: December 18, 1958

Card 3/3

YFADIKOLOPNA V. S.

MILLER, V.B.; LEVIN, P.I.; KONAREVA, G.P.; NEYMAN, M.B.; YENIKOLOPYAN, N.S.

Use of the kinetic isotopic method in the study of the oxidation  
of methane in the presence of nitromethane. Zhur.fiz.khim. 34  
no.9:1980-1986 S '60. (MIRA 13:9)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.  
(Methane) (Carbon--Isotopes)

74-101402-12/710, 10.5,

(b)  
Radiation-Induced Polymerization of Monomers in the Solid State

I. M. Barkalov, V. I. Gol'danskii, N. S. Likhovoyan,  
S. P. Yershova and G. M. Trushova

The authors investigated the kinetics of the radiation-induced polymerization of a number of vinyl monomers (acrylonitrile, methylmethacrylate, vinyl acetate, formaldehyde). The polymerization was carried out using 1.5 MeV electrons. The temperature range studied (from  $-196$  to  $0^{\circ}\text{C}$ ) included the melting point of the monomer. The temperature-dependence of the polymerization rate near the melting point changed in a variety of ways. The polymer yield in the solid phase reached a limiting value with increasing dose. The influence of phase transitions on the kinetics of polymerization was established. The results are interpreted on the basis of the theory developed and presented by N. N. Semenov at the International Symposium of Macromolecular Chemistry (Moscow, July 1960), and at the 18th Congress of Pure and Applied Chemistry (Montreal, August, 1961).

*Institute of Chemical Physics of the Academy of Sciences of the USSR, Moscow*

report presented at the 2nd Intl. Congress of Radiation Research,  
Harrogate/Yorkshire, Gt. Brit. 5-11 Aug 1962

YENIKOLOPYAN, N.S.; KONAREVA, G.P.

Homogeneous catalysis in the gas phase oxidation of hydrocarbons.  
Report No.2: Effect of nitromethane admixtures on the oxidation of  
methane. Izv. AN SSSR. Otd. khim. nauk no.2:230-235 F '61.

(MIRA 14:2)

1. Institut khimicheskoy fiziki AN SSSR.  
(Methane) (Oxidation)

KARMILOVA, L.V.; YENIKOLOPIAN, N.S.; NALBANDYAN, A.B.

Kinetics and mechanism of methane oxidation. Part 4: Effect  
of hydrogen peroxide and water on the reaction kinetics.  
Zhur. fiz. khim. 35 no.5:1046-1053 My '61. (MIRA 16:7)

1. Institut khimicheskoy fiziki AN USSR.  
(Methane) (Oxidation)  
(Chemical reaction, Rate of)

KARMILOVA, L.V.; YENIKOLOPYAN, H.S.; NALBANDYAN, A.B.; IL'IN, V.T.  
(Moskva)

Kinetics and mechanism of methane oxidation. Part 5:  
Constant rate of methane oxidation. Zhur. fiz. khim.  
35 no.7:1435-1442 J1 '61. (MIRA 14:7)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.  
(Methane) (Oxidation)

KARMILOVA, L.V.; YENIKOLOPYAN, N.S.

Kinetics and mechanism of methane oxidation. Part 6:  
Mechanism of carbon dioxide formation and the evaluation of  
the stationary state concentration of hydroxyl radicals in  
the reaction. Zhur. fiz. khim. 35 no.7:1458-1464 J1 '61.  
(MIRA 14:7)

1. AN SSSR, Institut khimicheskoy fiziki.  
(Methane) (Oxidation) (Carbon dioxide)



S/190/62/004/006/013/026  
B101/B110

AUTHORS: Dudina, L. A., Yenikolopyan, N. S.  
TITLE: Initiating mechanism in the thermal degradation of polymers  
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962,  
869-875

TEXT: A kinetic method is developed for judging whether the active centers in the thermal degradation of polymers are initiated by the "law of chance" or by the "law of terminal groups". For the degradation of the polymer to the monomer the following is written:  $dM/dt = K\epsilon$  ( $M$  = amount of monomer formed,  $K$  = effective constant of the reaction rate,  $\epsilon$  = amount of initial polymer).  $K \sim N_0^n$  ( $N_0$  = degree of polymerization).

The method suggested is based on determining the value and sign of  $n$ . According to R. Simha, L. A. Wall, in whose paper (J. Polymer Sci., 6, 39, 1951), the example of chain destruction is thoroughly discussed, the form of the function  $K = f(N_0)$  is determined as dependent on the course of reaction, and the following is found:  $n \leq 0$  for initiation by the law of terminal groups,  $n \geq 0$  for initiation by the "law of chance". The  
Card 1/2

Initiating mechanism in the ...

S/190/62/004/C06/013/026  
B101/B11C

uncertainty in the case  $n = 0$  can be eliminated by adding an inhibitor. The kinetics of degradation of polyformaldehyde (at  $222^{\circ}\text{C}$  in  $\text{N}_2$ ) and of polyformaldehyde treated with acetic anhydride was investigated experimentally. In both cases, a linear decrease of  $K$  was observed with increasing  $N_0$  (increasing  $\eta$ ) according to initiation by the law of terminal groups. There are 2 figures and 2 tables. The most important English-language reference is: H. H. G. Jellinek, Degradation of vinyl polymers, N. Y., 1955. ✓

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR)

SUBMITTED: April 8, 1961

Card 2/2

S/190/62/004/008/009/016  
B101/B180

AUTHORS: Bel'govskiy, I. M., Yenikolopyan, N. S., Sakhonenko, L. S.

TITLE: Determination of the molecular weight of polyformaldehyde by light scattering

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4; no. 8, 1962, 1197-1203

TEXT: An apparatus is described for measuring the intensity of the light scattered by solutions of polyformaldehyde in dimethyl formamide. One ray of a direct beam and one deflected through  $90^\circ$  in the dish containing the solution are photomultiplied and then compared by an electronic compensating circuit. With a thermostat allows, temperatures up to  $200^\circ\text{C}$  can be used. A differential refractometer is also described for determining the increment at temperatures up to  $200^\circ\text{C}$ . At  $150^\circ\text{C}$  density =  $0.845 \text{ g/cm}^3$ ; refractive index  $n_D^{25} = 1.390$ ; Rayleigh constant  $R_{90}^u = (44.0 \pm 1.5) \cdot 10^{-6} \text{ cm}^{-1}$ . Light scattering increased linearly with polyformaldehyde concentration. The molecular weight was determined

Card 1/2

Determination of the molecular weight ... S/190/62/004/008/009/016  
B101/B180

viscosimetrically as a function of the intrinsic viscosity:

$[\eta] = 4.4 \cdot 10^{-4} M^{0.66}$  which yielded molecular weights between  $89 \cdot 10^3$  and  $285 \cdot 10^3$ . The molecular weights determined by light scattering were not consistent with the viscosimetric values. Light scattering only yields a weight - average molecular weight. There are 10 figures and 2 tables. The most important English-language reference is: T. A. Koch, P. E. Lindvig, J. Polymer Sci., 1, 9, 164, 1959.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR)

SUBMITTED: May 12, 1961

Card 2/2

S/190/62/004/012/002/015  
B101/B106

AUTHORS: . Skuratov, S. M., Yenikolopyan, N. S., Bonetskaya, A. K.,  
Voyevodskiy, V. V.

TITLE: Mechanism of lactam polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962,  
1770-1778

TEXT: In continuation of papers of 1952-54 (last publication Dokl. AN SSSR, 95, 1017, 1954), the polymerization of  $\epsilon$ -caprolactam and  $\gamma$ -enantholactam was studied in the presence of water, water and acid, and water and alkali at 231.5°C. A slightly modified reaction scheme is proposed on the basis of experimental results concerning induction period, maximum reaction rate, time before maximum reaction rate is reached, degree of conversion, heat

effect of the reaction: (1)  $B + H_2O \xrightleftharpoons[k_1]{k_1} AH$ ; (2)  $AH + AH \xrightarrow{k_2} P + H_2O$ ;

(3)  $AH + P \xrightarrow{k_3} P + H_2O$ ; (4)  $AH + B + X \xrightarrow{k_4} P + X$ ; (5)  $B + P \xrightarrow{k_5} P$ ;

Card 1/3

S/190/62/004/012/002/015  
B101/B186

Mechanism of lactam...

(6)  $B + H_2O + X \xrightarrow{k_6} AH + X$ ; (7)  $AH + X \xrightarrow{k_7} B + H_2O + X$ ; where B = lactam, AH = amino acid, P = polyamide, X = catalyst. The probable course of these reactions under different conditions is discussed, and the following equations are derived for the rate of polymerization, w: (A) for polymerization of  $\epsilon$ -caprolactam in the presence of  $H_2O$ :  $w = \alpha' [H_2O] [B] ([B_0]^2 - [B]^2)$ , where  $\alpha' = k_4 k_6 / 2k_7$ ; (B) for polymerization of  $\gamma$ -enantholactam in the presence of water:  $w = \alpha' [H_2O] [B] \sqrt{[B_0]^2 - [B]^2}$ ; where  $\alpha' = k_5^{0.5} k_2^{0.5} k_6 / k_3$ ; (C) for polymerization of  $\epsilon$ -caprolactam in the presence of  $H_2O$  and  $H_3PO_4$ :  $w = \beta' \sqrt[4]{[AcH] [B]} \sqrt{[B_0]^2 - [B]^2}$ , where  $\beta' = (k_4 k_5 k_6 [H_2O] / k_7)^{0.5}$ , and AcH = acid; (D) for polymerization of  $\gamma$ -enantholactam in the presence of  $H_2O$  and  $H_3PO_4$ :  $w = \alpha' \sqrt[4]{[AcH] [B]} \sqrt{[B_0]^2 - [B]^2}$ , where  $\alpha' = k_2^{0.25} k_5^{0.75} k_6^{0.5} [H_2O]^{0.5} / k_3^{0.5}$ ; (e) in the polymerization of  $\epsilon$ -caprolactam and  $\gamma$ -enantholactam in the presence of  $H_2O$  and NaOH, the presence of

Card 2/3

Mechanism of lactam...

S/190/62/004/012/002/015  
B101/B186

NaOH only reduces the induction period without affecting the polymerization kinetics proper. All the experimental results are satisfactorily explained by these equations. There are 3 tables.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova  
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: June 24, 1962

Card 3/3

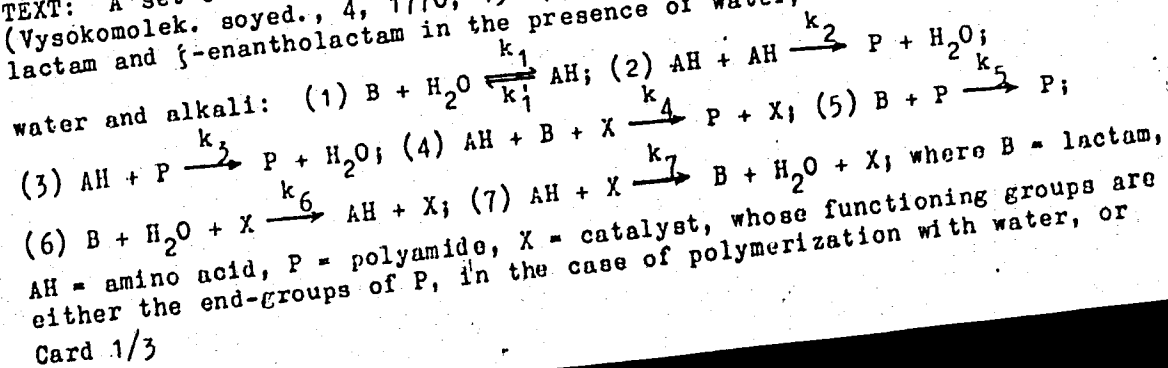
S/190/62/004/012/003/015  
B101/B186

AUTHORS: Yenikolopyan, N. S., Bonetskaya, A. K., Skuratov, S. M.

TITLE: Induction period of  $\epsilon$ -caprolactam and  $\gamma$ -enantholactam polymerization under various conditions

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962, 1779-1783

TEXT: A set of reaction equations was drawn up in a previous paper (Vysokomolek. soyed., 4, 1770, 1962) for the polymerization of  $\epsilon$ -caprolactam and  $\gamma$ -enantholactam in the presence of water, water and acid, and water and alkali:





S/190/62/004/012/003/015  
B101/B186

Induction period of...

$H_3O^+$  ion in the case of polymerization in the presence of acid. In the present paper, the experimental data are used for deriving equations for the induction period as dependent on the amount of  $H_2O$  added. Reaction (1) catalyzed by the amino acid gives rise to:  $B + H_2O + AH \xrightarrow{k_1} AH + AH$ . The induction period  $t = (1/\varphi) \ln w/\alpha$ ; where  $w = \alpha e^{\varphi t}$ ,  $\alpha = k_5'k_1[B]/k_1'$ , and  $\varphi = k_1'[B][H_2O]$ . In agreement with the experiment, the induction period is inversely proportional to the amount of water added. The induction period decreases with an increased addition of NaOH. In this case, the cooperation of the hydroxyl ion must be taken into account besides reaction (1) and the catalysis by the amino acid:  $B + H_2O + OH^- \xrightarrow{k_1''} AH + OH^-$ . Hence,  $t = (1/\varphi)(\ln w - \ln \alpha)$ , where  $\varphi = k_2'[B][H_2O]$ ,  $\alpha = k_5'k_1''[B][OH^-]/k_1'$ . Consequently, the kinetics of polymerization proposed interprets the reaction courses correctly. There are 2 figures and 1 table.

Card 2/3

Induction period of...

S/190/62/004/012/003/015  
B101/B186

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova  
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: June 24, 1961

Card 3/3

L 12438-63

EWP(j)/EPF(c)/EWT(m)/BDS ASD Pc-4/Pr-4 RM/WW

ACCESSION NR: AP3001159

S/0190/63/005/006/0861/0867

65  
63

AUTHOR: Dudina, L. A.; Yenikolopyan, N. S.

TITLE: Thermal and thermo-oxidative degradation of polyformaldehyde. 1. Order of the thermal degradation reaction

SOURCE: Vy\*sokomolekulyarny\*ye soyedineniya, v. 5, no. 6, 861-867

TOPIC TAGS: thermal degradation, thermo-oxidative degradation, degradation reaction, polyformaldehyde, activation energy

ABSTRACT: The polymers used in the study were prepared by polymerization of formaldehyde in toluene, using calcium stearate as initiator. A part of the polymer was stabilized by heating at 100C for three hours with acetic anhydride. The molecular weights of the nonstabilized polymers were  $2.57 \times 10^5$  and  $3.16 \times 10^5$ , and  $1.38 \times 10^5$  for the stabilized polymer. Thermal destruction was conducted in a vacuum installation at  $10^{-4}$  mm residual pressure, at temperatures varying from 120 to 346C, and the volume of liberated gas was determined by pressure change. Such a method is applicable where the sole gaseous product is a monomer, and the authors were able to show that it fitted their case by obtaining pressure readings almost matching theoretical ones. The semilogarithmic

Card 1/2

L 12438-63

ACCESSION NR: AP3001159

2

anamorphoses of kinetic decomposition curves of alpha-polyoxymethylene and the non-stabilized polyformaldehyde are curved, while those of the stabilized polymer form a straight line, indicating that in the latter instance the decomposition of the polymer follows a first order course. It implies that here the activation energy of active center destruction is less than the activation energy of monomer elimination. A part of the experiment was conducted by O. M. Koz'miny\*kh. Orig. art. has: 15 formulas, 3 charts, and 1 table.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, Academy of Sciences SSSR)

SUBMITTED: 30Nov61

DATE ACQ: 01Jul63

ENCL: 00

SUB CODE: 00

NO REF SOV: 004

OTHER: 004

Card 2/2

SEMENOV, N. N., akademik (Moskva); YENIKOLOPYAN, N. S. (Moskva)  
GOL'DANSKIY, V. I. (Moskva)

On the problem of polymerization at low temperatures.  
Rev chimie 7 no. 1: 501-511 '62.

1. Institut khimicheskoy fiziki AN SSSR, Moskva.

36055

S/063/62/007/002/007/014  
A057/A126

15.8090

AUTHORS: Yenikolopyan, N.S., Doctor of Chemical Sciences, Vardanyan, M.S.

TITLE: The production of polyformaldehyde

PERIODICAL: Zhurnal vsesoyuznogo khimicheskogo obshchestva imeni D.I.  
Mendeleyeva, v. 7, no. 2, 1962, 194 - 200

TEXT: Properties, the production, and the mechanism of polymerization of polyformaldehyde are discussed and some experimental results are presented. A great part of the presented information is apparently taken from the Symposium on Macrochemistry in Canada, 1961. Polymers of formaldehyde are known since their discovery by A.M. Butlerov. Two types - polyoxaldehydes and polyoximethylenes can be noted. High molecular weight polyoximethylene, i.e., polyformaldehyde, shows some outstanding physical and chemical properties, thus being of interest for various purposes. Monomer formaldehyde used as initial material can be prepared: 1) as low-molecular compound, para-formaldehyde and  $\alpha$ -polyoximethylene; 2) as semi-acetal; or 3) by partial condensation. The monomer should contain less than 0.001% admixtures. Preliminary polymerization, or filtration through molecular filters allows to remove the impurities below 0.001%. The purified

Card 1/3

The production of .....

S/063/62/007/002/007/014  
A057/A:26

monomer can be polymerized in two ways in the presence of various catalysts. The latter is not consumed during polymerization, i.e., active centers are not lost. The effect of  $H_2O$ ,  $CH_3OH$ ,  $HCOOH$ ,  $CH_3COOH$ ,  $(CH_3CO)_2O$ ,  $CO$ ,  $CO_2$ , and other substances on rate and degree of polymerization was investigated experimentally. In contrast to the  $OH^-$  ions, the  $HCO_3^-$  and  $HCOO^-$  ions do not influence the polymerization of formaldehyde. Thus, in principle, a regulation of the process and reproduction of polyformaldehyde with any desired molecular weight is possible. The stability of para-formaldehyde against heat and oxidation depends only on the nature of the end-group of the chain. The present authors demonstrate that at thermal destruction also processes of chain transfer to the polymer are of importance as well as to the evolving monomer formaldehyde, simultaneously with generation, growth and rupture of chains. Studies of the kinetics of thermal destruction of polymers with  $OH$  and  $OCOCH_3$  end-radicals showed that the different rate of destruction depends upon the different activation energy. It was proved experimentally that oxygen increases sharply the destruction rate, and decreases even more the molecular weight. However, the molecular weight of acetylated polymer decreases much slower than that of the non-stabilized polymer. This indicates that oxygen does not attack directly the middle of the chain. Oxygen apparently does not attack directly the polymer chain, but the evolved monomer

Card 2/3

The production of ....

S/063/62/007/002/007/014  
A057/A126

formaldehyde. The observed greater mutual effect of oxygen and formic acid is not explained yet. An efficient mixture of a stabilizer should be able to bind the evolving formaldehyde (limiting thus its further oxidation), also the evolving formic acid, and contain radical inhibitors retaining the chain process of destruction. There are 9 figures.

Card 3/3

X



KOZLOV, P.V., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.;  
DOLGOPLOSK, V.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN,  
V.A., red.; KOLESNIKOV, G.S., red.; KOROTKOV, A.A., red.;  
KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S.,  
red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.;  
SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N.,  
red.; FREYMAN-KRUPENSKIY, D.A., tekhn. red.

[Adhesion of polymers] Adgeziia polimerov; sbornik statei.  
Moskva, Izd-vo AN SSSR, 1963. 142 p. (MIRA 16:10)  
(Polymers) (Adhesion)

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPLOSK, B.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTECV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, D.A., tekhn. red.

[Heterochain high-molecular weight compounds] Geterotsepnnye vysokomolekuliarnye soedineniia; sbornik statei. Moskva, Izd-vo "Nauka," 1963. 246 p. (MIRA 17:3)

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPLOSK, B.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTKOV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, K.A., tekhn. red.

[Carbochain high-molecular weight compounds] Karbotsepnnye vysokomolekuliarnye soedineniia; sbornik statei. Moskva, Izd-vo AN SSSR, 1963. 287 p. (MIRA 17:1)

ACCESSION NR: AT4020701

S/0000/63/000/000/0100/0106

AUTHOR: Bel'govskiy, I. M.; Kravchuk, I. P.; Nikol'skiy, V. G.; Yenikolopyan, N. S.

TITLE: Low-temperature radiation-induced polymerization of isobutylene

SOURCE: Karbotsepnyye vy\*sokomolekulyarnyye soyedineniya (Carbon-chain macromolecular compounds); sbornik statey. Moscow, Izd-vo AN SSSR, 1963, 100-106

TOPIC TAGS: polymerization, radiation polymerization, Isobutylene, low-temperature polymerization

ABSTRACT: In order to clarify the degree to which the reaction proceeds via an ionic mechanism, the kinetics of the radiation polymerization of isobutylene over a temperature range of -40 to -196C were investigated. With respect to low-temperature radiation polymerization, the following conclusions could be drawn: The independence of the polymerization yield of the intensity of the dose indicates a linear relationship between the polymerization rate and the radiation intensity. The polymerization of isobutylene in the liquid phase is accelerated by a decrease in temperature down to the freezing point of the monomer. The reaction rate has an activation energy of 2.5 kcal/mol. In the solid phase, the reaction rate has a normal temperature dependence with an apparent activation energy of

Card 1/2

ACCESSION NR: AT4020701

+1.88 kcal/mol. The maximum rate of polymerization is obtained in the initial stage of irradiation and the process shows a tendency to become saturated as the dose of radiation is increased. The molecular weight of the product has a maximum value during the initial stage of irradiation, after which it drops rapidly to a value of 15,000-20,000; thereafter it is essentially independent of the dose. Orig. art. has: 5 formulas and 5 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AN SSSR)

SUBMITTED: 26Apr62

DATE ACQ: 20Mar64

ENCL: 00

SUB CODE: OC

NO REF SOV: 005

OTHER: 005

Card 2/2

YENIKOLOPYAN, N.S.; SHILOV, A.Ye.

"Chemical kinetics and catalysis" by G.M.Panchenkov,  
V.P.Lebedeva. Reviewed by N.S.Enikolopian, A.E.Shikov.  
Kin.i kat. 4 no.2:322-325 Mr-Apr '63. (MIRA 16:5)  
(Chemical reaction, Rate of)(Catalysis)  
(Panchenkov, G.M.) (Lebedev, V.P.)

DUDINA, L.A.; YENIKOLOPYAN, N.S.

Thermal and thermal oxidation degradation of polyformaldehyde.  
Part 1: Order of the thermal degradation reaction. Vysokom.sped.  
5 no.6:861-867 Je '63. (MIRA 16:9)

1. Institut khimicheskoy fiziki AN SSSR.  
(Formaldehyde) (Degradation)

ACCESSION NR: AP3003787

S/0190/63/005/007/0986/0993

AUTHORS: Dudina, L. A.; Yanikolopyan, N. S.

TITLE: Thermal and thermooxidative degradation of polyformaldehyde. 2. On temperature dependence of thermal degradation rate

SOURCE: Vy\*sokomolekulyarny\*ye soyedineniya, v. 5, no. 7, 1963, 986-993

TOPIC TAGS: thermal dissociation, dissociation rate, unstabilized polyformaldehyde, activation energy, true activation energy, chemical reaction, reaction rate constant

ABSTRACT: The thermal dissociation of polymers upon heating was investigated, using the method described by the authors in (Vy\*sokomolek. soyed. 5, 861, 1963). The polymer specimen was in the form of a tablet with heat being applied from its base. At high temperatures (above 260C) the dissociation rate of unstabilized polyformaldehyde (PFA) was found to be independent of the temperature. In the temperature range 190-260C the dissociation activation energy of PFA in the 0.02 gm specimen yielded a value of  $17 \pm 1$  kcal/mol, and for the 0.05 gm specimen,  $13 \pm 1$  kcal/mol. An analytic method has been developed to determine the true activation

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ACCESSION NR: AP3003787

energy in the chemical reaction when the limiting factor in the heat treatment is the internal conductivity of the specimen. The effective reaction rate constant is expressed by

$$k_{\text{eff}} = \frac{S}{L} \sqrt{\frac{2k_0\lambda}{Q}} \frac{E}{R} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{n!}{(E/RT_0)^{n+1}} e^{-E/RT_0}$$

where  $\lambda$  - thermal conductivity,  $\rho$  - density,  $S$  - cross-sectional area,  $E$  - activation energy,  $k_0$  - constant in heat source term

$$Q' = -Qk_0\rho e^{-E/RT_0}$$

The effective activation rate constant is then plotted against the inverse specimen weight. It is shown that when the apparent rate constant is inversely proportional to the sample, the true activation energy is twice that of the experimental value. The activation energy of the stabilized polymer terminated with the hydroxyl group yields a value of 26 kcal/mol and with acetylene,  $E = 32$  kcal/mol. "The authors express their gratitude to A. S. Kompaneyets for evaluating the work." Orig. art. has: 13 equations and 3 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AN SSSR)

Card 2/2 2

L 15608-63

RPR/ENP(j)/EPF(c)/ENT(m)/BDS--AFFIC/ASD--Fe-4/Pe-4/Pr-4--

RH/WN/JW

ACCESSION NR: AP3004699

S/0190/63/005/008/1135/1139

AUTHORS: Dudina, L. A.; Yenikolopyan, N. S.

TITLE: Thermal and thermooxidative decomposition of polyformaldehyde. 3. Chain transfer reaction in thermal decomposition 7

SOURCE: Vyssokomolekulyarnyye soyedineniya, v. 5, no. 8, 1963, 1135-1139

TOPIC TAGS: formaldehyde polymer, alpha-polyoxymethylene, thermal decomposition, chain transfer, stabilization

ABSTRACT: This report is a continuation of earlier studies by the authors on thermal decomposition of formaldehyde polymers. An explanation was sought for the deviation of the decomposition rate from that of a first order reaction. The method used was described in an earlier publication by the authors (Vyssokomolek., 5, 986, 1963), the kinetics of the reaction being evaluated on the basis of gas rate evolution from polyformaldehyde samples at 130-280°C in a closed system. It was found that the rate of monomeric HCOH evolution in nonstabilized specimens tapered off within 5 to 10 minutes, a phenomenon not observed in control tests in an atmosphere of nitrogen, thus excluding pressure as a potential factor of

Card 1/2

L 15608-63

ACCESSION NR: AP3004699

2  
 repolymerization. On the other hand, where the polyformaldehyde samples were stabilized by acetic anhydride, the rate of monomeric HCOH evolution proceeded independently from pressure, while the molecular weight of the polymer continued to decrease. A theory is advanced suggesting the formation of fragments with acetyl end-groups by means of a chain-transfer reaction. The experimental work on the decomposition of alpha-polyoxymethylene was conducted by O. M. Koz'minyakh. Orig. art. has: 1 formula and 5 charts.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, Academy of Sciences, SSSR)

SUBMITTED: 20Dec61

DATE ACQ: 28Aug63

ENCL: 00

SUB CODE: CH

NO REF SOV: 003

OTHER: 002

Card 2/2

L 15605-63

EPR/EWP(j)/EPF(c)/EWT(m)/BDS AFFTC/ASD Ps-4/Pr-4/Pc-4

RM/WW/JW

ACCESSION NR: AP3004703

8/0190/63/005/008/1160/1164

AUTHORS: Dudina, L. A.; Karmilova, L. V.; Yenikolopyan, N. S.

TITLE: Thermal and thermooxidative decomposition of polyformaldehyde. 4. Kinetics of the thermooxidative reaction

SOURCE: Vyssokomolekulyarnyye soyedineniya, v. 5, no. 8, 1963, 1160-1164

TOPIC TAGS: formaldehyde, polyformaldehyde, thermooxidative decomposition, auto-catalysis, stabilization

ABSTRACT: The polymer (0.382 gms) was placed in a glass dish attached to a quartz spiral suspended inside a glass cylinder. Through this a stream of oxygen was passed at temperatures ranging from 165-220C. The changes in weight of the sample were followed by recording the extension of the spiral. The gaseous decomposition products, trapped by means of condensation at temperatures down to -80C, were analyzed for monomeric formaldehyde, organic peroxides, hydrogen peroxide, and formic acid. The viscosities of the samples were determined by Ubbelohde's method in dimethylformamide solution at 150C, and from it the molecular weights were calculated. It was found that the oxidative decomposition of

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L 15605-63

ACCESSION NR: AP3004703

2

nonstabilized polyformaldehyde proceeds at a rate nearly 50 times greater than purely thermal decomposition<sup>1</sup> in an atmosphere of argon, formaldehyde being the only decomposition product. Also, in the oxidative process the molecular weight of the residual polyformaldehyde shows a nearly instant drop in molecular weight to  $2.6 \cdot 10^3$  from an initial figure of  $3 \cdot 10^5$ , while in an atmosphere of argon the molecular weight is affected only slightly. Experiments with polyformaldehyde stabilized by means of acetic anhydride revealed a rapid slowing of the decomposition reaction and an insignificant drop in molecular weight. It is suggested that the polyformaldehyde decomposition process possesses autocatalytic characteristics. Orig. art. has: 6 charts.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Physical Chemistry, Academy of Sciences, SSSR)

SURMITTED: 05Jan62

DATE ACQ: 28Aug63

ENCL: 00

SUB CODE: CH

NO REF SOV: 005

OTHER: 002

Card 2/2

L 15601-63 EPR/EWP(j)/EPF(c)/EWT(m)/BDS ASD Ps-4/Pc-4/

Pr-4 RM/WM/JW

ACCESSION NR: AP3004710

S/0190/63/005/008/1245/1249

AUTHORS: Dudina, L. A.; Agayants, L. A.; Karmilova, L. V.; Yenikolopyan, N. S.

TITLE: Thermal and thermooxidative decomposition of polyformaldehyde. 5. The role of formic acid in the thermooxidative reaction

SOURCE: Vy\*sokomolekulyarny\*ye soyedineniya, v. 5, no. 8, 1963, 1245-1249

TOPIC TAGS: thermal decomposition, thermooxidative decomposition, polyformaldehyde, formic acid, stabilization

ABSTRACT: Experiments were conducted using 0.382 gm of acetylated polyformaldehyde having a molecular weight of  $0.7 \cdot 10^5$ , which was subjected to vapors of 85% formic acid in a current of oxygen or argon, or to the acid alone. The kinetics of polyformaldehyde decomposition were recorded in an earlier paper by L. A. Dudina, L. V. Karmilova, N. S. Yenikolopyan (Vy\*sokomolek. soed., 5, 1160, 1963). It was found that at 220C the rate of thermooxidative decomposition of polyformaldehyde in argon increases in proportion to the formic acid gas content and that an almost double rate and volume of destruction take place in the presence of oxygen. Where samples of polyformaldehyde were reacted with liquid 85%

Card 1/2

L 15601-63

ACCESSION NR: AP3004710

formic acid previous to exposure to oxygen or argon; it was observed that at 202C the rate of decomposition in oxygen was tenfold that in argon. The volume of polyformaldehyde decomposition in argon did not exceed 4%, and the viscosity went down to only 0.62 from an original 0.68. It is concluded that formic acid reacts with polyformaldehyde so as to facilitate its subsequent thermooxidative decomposition by oxygen. Orig. art. has: 1 formula, 4 charts, and 2 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, Academy of Sciences, SSSR)

SUBMITTED: 08Feb62

DATE ACQ: 28Aug63

ENCL: 00

SUB CODE: CH

NO REF SOV: 002

OTHER: 001

Card 2/2

PROSHLYAKOVA, N.F.; SANAYA, I.F.; YENIKOLOPYAN, N.S.

Polymerization of formaldehyde. Part 1: Order of the reaction in  
anionic polymerization. Vysokom.sped. 5 no.11:1632-1637 N '63.  
(MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.



IRZHAK, V.I.; ROMANOV, L.M.; YENIKOLOPYAN, N.S.

Polymerization of formaldehyde. Part 2: Effect of a monomer on  
the mean degree and rate of polymerization. Vysokom.sped. 5  
no.11:1638-1640 N '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

BOBKOVA, L.P.; KORSAKOV, V.S.; ROMANOV, L.M.; YENIKOLOPYAN, N.S.

Polymerization of formaldehyde. Part 3: Effect of active addition agents on the polymerization of formaldehyde in solutions.  
Vysokom.sped. 5 no.11:1653-1657 N '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

PROSHLYAKOVA, N.F.; SANAYA, I.I.; YENIKOLOPYAN, N.S.

Polymerization of formaldehyde. Part 4: Change in molecular weight of polyformaldehyde in the course of polymerization. Vysokom. soed. 5 no.12:1776-1779 D '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

BOBKOVA, L.P.; KORSKOV, V.S.; ROMANOV, L.M.; YENIKOLOPYAN, N.S.

Polymerization of formaldehyde. Part 5: Effect of water, methyl alcohol, acetic acid, and acetic anhydride on the polymerization of formaldehyde in solutions. Vysokom. soed. 5 no.12:1780-1784 D '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

L 12984-63 EWP(j)/EPF(c)/EWT(m)/BDS ASD PC-4/Pr-4 RM/WW  
 ACCESSION NR: AP3000517 S/0020/63/150/002/0309/0312

65  
 64

AUTHOR: Dudina, L. A.; Karmilova, L. V.; Yenikolopyan, N. S.

TITLE: Oxidative destruction of polyformaldehyde

SOURCE: AN SSSR. Doklady, v. 150, no. 2, 1963, 309-312

TOPIC TAGS: thermal oxidative destruction, polyformaldehyde, depolymerization, activation energy, reaction rate

ABSTRACT: Thermal oxidative destruction of polyformaldehyde with hydroxyl or with acetylenic end groups was carried out at 180-185 degrees; condensed products were continuously collected and analyzed. Regardless of the end group, main products were monomeric formaldehyde (about 80-90%) and formic acid (5-8%), with traces of others, but no peroxides. The course of the O-initiated depolymerization and practical absence of oxidation reaction was studied. Activation energies and reaction rates were calculated for proposed reactions where the molecule can disintegrate as shown in equation (1) of enclosure 1, or it can add a molecule of O as shown in equation (2) of enclosure 1, then subsequently isomerize. However, peroxides were not detected: either they were not formed according to proposed reactions, or additional reactions, not calculated herein, are involved. Also none of the proposed reactions explains the formation of formic acid. Further study is recommended.

Card 1/1 Association: Inst. of Chemical Physics, Academy of Sciences SSSR

L 12335-63

ACCESSION NR: AP3000753

EPR/EWP(j)/EPF(c)/EWT(m)/EDS AFFTC/ASD Ps-4/Pc-4/Pr-4 EM/NW  
S/0020/63/150/003/0580/0583 73  
72

AUTHOR: Dudina, L. A.; Berlin, Al. Al.; Karmilova, L. V.; Yenikolopyan, N. S.

TITLE: Changing the molecular weight by oxidative destruction of polyformaldehyde

SOURCE: AN SSSR. Doklady, v. 150, no. 3, 1963, 580-583

TOPIC TAGS: oxidative destruction, polyformaldehyde

ABSTRACT: In continuation of earlier work by L. A. Dudina, L. V. Karmilova, and N. S. Yenikolopyan (DAN. 150, no. 2, 1963), a study was made to determine whether the O-initiated decomposition of polyformaldehyde does indeed go according to the equation shown in the enclosure. Experimentally a sharp drop in molecular weight was found, such that its dependence on the degree of conversion is representative of the formation of two stable fragments upon decomposition of the molecule. These fragments could be formed either because the O inhibits decomposition of the active center in addition to initiating destruction of the polymer or because of acidolysis of the polymer by the acid from the oxidation process. Calculations also indicated that the above-proposed reaction does not account for the drop in molecular weight. Orig. art. has: 1 figure and 28 equations.

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BARKALOV, I.M., GOLDANSKIY, V.I., YENIKOLOPYAN, M.S., TROPIMOVA, G.M.,  
TEREKHOVA, S.P.

Radiation-induced solid-state polymerisation.

Part I..Polymerisation of acrylonitrile.

Part II..Polymerisation of vinyl acetate.

Various kinds of polymerisation rate temperatures dependences.

Report submitted for the International Symposium of Macromolecular chemistry,  
Paris, 1-6 July 63





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ACCESSION NR: AP4009152

activation energy of the solid phase polymerization. From -196 to -150°C a yield

SUB CODE: CC, MP

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BRUNOVSKIY, I.M.; KOLCHVICH, K.I.; YAKHOLSKY, N.S.

Kinetics of radical polymerization by the light scattering  
method. Part 2: Unsteady reaction. Vysokom. soob. 6 no. 5:  
371-376 by '64. (Rus. 17:6)

1. Institut khimicheskoy fiziki AN SSSR.